PB86-134053

Hyperfiltration for Textile Preparation Caustic Discharge Reduction

CARRE, Inc., Seneca, SC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Dec 85

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completin

1. REPORT NO. EPA/600/2-85/139	2.	3. R PB86-134053
4. TITLE AND SUBTITLE Hyperfiltration for Textile Preparation Caustic Discharge Reduction		5. REPORT DATE December 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Craig A. Brandon		8. PERFORMING ORGANIZATION REPORT NO. CARRE No. 100
9. PERFORMING ORGANIZATION NAME AND ADDRESS CARRE, Inc. 109 Debra Street Seneca, South Carolina 29679		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. CR810188
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 7/82 - 11/83 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is John S. Ruppersberger, Mail Drop 54, 919/541-2734.

16. ABSTRACT The report gives results of a study, joining a hyperfiltration (HF) system with an operating caustic scour and preparation range in an integrated textile dye and finishing plant. (HF is a membrane separation technique widely used in desalination of natural water and in some industrial separation applications. Because energy, process chemicals, and water are discharged from industrial processes in large quantities, recycle has been studied with the objectives of energy and material conservation and pollution abatement. The results of several research projects with formed-in-place membranes are the background for the current project.) The effluent treated by HF is a 3-10 wt % caustic (NaOH) solution. The caustic percentage and the amounts and types of cantaminants in the effluent depend on the style and weight of fabric being processed. Results of this prototype project indicated a positive rate of return, with savings of about $379,900/yr, greatly exceeding the installed capital ($361,500) and operating ($37,900/yr) costs. The prototype unit is being expanded from 100 to 210 sq m. A second 220 sq m HF unit is also being installed. The report describes the applicable textile process, the reuse scenario, and the HF unit and its operation.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Circulation	Pollution Control	13B	
Filtration	Scouring	Stationary Sources	07D	
Textile Finishing	Fluid Filters	Filter Separation	13H	13K
Textile Industry	Membranes	Hyperfiltration	11E	11G
Waste Water				
Water Treatment				

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

PB86-134053

EPA/600/2-85/139
December 1985

HYPERFILTRATION FOR TEXTILE PREPARATION CAUSTIC DISCHARGE REDUCTION

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Hyperfiltration (HF) is a membrane separation technique widely used in desalination of natural water and in some industrial separations applications. Because energy, process chemicals and water are discharged from industrial processes in large quantities, recycle has been studied with the objectives of energy and material conservation and pollution abatement. The results of several research projects with formed-in-place membranes are the background for the current project, which is the joining of an HF system with an operating caustic scour and preparation range in an integrated textile dye and finishing plant. The effluent treated by HF is a 3 to 10 weight percent caustic (NaOH) solution. The caustic percentage and the amount and type of contaminants in the effluent depend upon the style and weight of fabric being processed.

HF membranes formed on porous sintered steel tubular supports are used to remove contaminants from a hot (95°C) caustic scour solution and render it reusable for scouring. For this demonstration over 15 million meters of approximately 1.5 meter wide fabric have been scoured using over 3 million liters of recycled caustic solution. The initial prototype unit has been replaced with an improved design using all 316L stainless steel porous material to achieve the necessary corrosion resistance.

The results of this prototype project indicated a positive rate of return with savings of $379,900 per year and installed capital cost of $361,500 and operating costs of $37,900 per year. The prototype unit has been expanded from 100 to 210 square meters of membrane area and a second 220 square meter unit is also being installed. Start-up for both units is scheduled for late 1985.

This report describes the applicable textile process, the reuse scenario and the HF unit and its operation.

TABLE OF CONTENTS

ABSTRACT..... iii

TABLE OF CONTENTS..... v
FIGURES..... vi
TABLES..... vi
METRIC CONVERSIONS..... vii
ACKNOWLEDGEMENTS..... viii
GLOSSARY..... ix

Section

1 INTRODUCTION
- HYPERFILTRATION..... 2
- PREVIOUS STUDIES..... 2
- PURPOSE AND SCOPE..... 3
- METHOD OF STUDY..... 3

2 CONCLUSIONS AND RECOMMENDATIONS..... 5

3 TEXTILE PROCESS DESCRIPTION
- PREPARATION RANGE EQUIPMENT AND FUNCTION..... 6
- CAUSTIC FLOW SCHEMATIC..... 8
- PRODUCTION..... 10
- EFFLUENT CHARACTERISTICS..... 10

4 RECOVERY SYSTEM
- SYSTEM SCHEMATIC DIAGRAM..... 12
- HF MEMBRANE ARRANGEMENT..... 14
- OPERATION MODES..... 14
- RECYCLE..... 14
- CLEANING..... 16

5 PROJECT RESULTS
- MEMBRANE AND EQUIPMENT PERFORMANCE..... 17
- CHEMICAL CHARACTERISTICS OF RECYCLED PERMEATE... 17
- MEMBRANE FLUX..... 22
- MEMBRANE CLEANING..... 25
- EQUIPMENT OPERATING HISTORY AND AVAILABILITY.... 25
- ABILITY TO REUSE CAUSTIC..... 27
- EFFECT OF REUSE ON FABRIC..... 27
- COST EVALUATION..... 27

REFERENCES..... 31

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LIST OF FIGURES

Figure		Page
1.	Preparation Range No. 4.....	7
2.	Caustic Flow on the Preparation Range Without Recovery System Interaction.....	9
3.	Recovery System Interaction with Scour Unit.....	13
4.	HF Membrane Arrangement.....	15
5(a).	Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken Prior to Recovery System Operation.....	18
5(b).	Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken Prior to Recovery System Operation.....	19
6(a).	Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken During Recovery System Operation.....	20
6(b).	Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken During Recovery System Operation.....	21
7.	Fouling Rates versus Production Style.....	24

LIST OF TABLES

Table		Page
1.	Chemical Characteristics of Scour Saturator Overflow Effluent.....	11
2.	Performance During Selected Five-Day Period.....	23
3.	Membrane Cleaning Procedure.....	26
4.	Fabric Extract Chemical Analyses Results.....	28
5.	Annual Savings for Recycle of 40 Liters/Min. of Caustic (6% NaOH).....	29
6.	Capital and Operating Costs for Recycle of 40 Liters/Minute of Caustic.....	30

ENGLISH-METRIC CONVERSION TABLE*

To Convert From	To	Multiply by
Inch	Meter	2.54×10^{-2}
Feet	Meter	3.05×10^{-1}
Square inch	Square meter	6.45×10^{-4}
Square feet	Square meter	9.29×10^{-2}
Cubic feet	Cubic meter	2.83×10^{-2}
Gallon	Cubic meter	3.79×10^{-3}
Pound	Kilogram	4.54×10^{-1}
Pound per square inch (psi)	Paschals	6.89×10^{3}
Horsepower (Hp)	Watt	7.46×10^{2}
Gallon per day	Cubic meter per day	3.79×10^{-3}
Gallon per minute (GPM)	Cubic meter per day	5.45
Gallon per square foot-day (GFD)	Cubic Meter per square meter-day	4.10×10^{-2}

*The units most familiar to the projected readership of this report have been maintained.

ACKNOWLEDGEMENTS

This study was conducted as a cooperative effort with major contributions made by a number of people. The cooperation and assistance of the Graniteville staff members is particularly acknowledged: Lawton Johnston, Lewis Ready, Archie Coleman.

CARRE, Inc. provided overall program management and engineering and chemistry support. Staff members at CARRE, Inc. making major contributions are C. A. Brandon, J. L. Gaddis, H. G. Spencer, Donald K. Todd, Daniel A. Jernigan and Steven C. Brandon.

This demonstration benefited from the guidance of Robert V. Hendriks, U. S. Environmental Protection Agency, as Principal Project Officer.

GLOSSARY

CONCENTRATE - the fluid that does not permeate the membrane and thus contains the solute species that do not pass through the membrane.

FLAME SINGEING - an open flame is maintained near the surface of the moving fabric as it enters the preparation range to singe (burn) short fibers that extend above the plane of the surface of the fabric.

FLUX - the volume of permeate generated per unit of membrane area per unit of time.

HYPERFILTRATION - a membrane separation process operating on the principle of selective diffusion through a semi-permeable membrane achieved by pressure differential.

HYPERFILTRATION (HF) UNIT - a component of the recovery system consisting of ZOPA membranes arranged in a Single Pass configuration.

MEMBRANE FOULING - a decrease in flux that is not an instantaneously reversible effect of controlled operating variables. Fouling is usually categorized as (1) an alteration in the membrane due to a chemical reaction with the waste stream components or (2) an accumulation of a deposited material.

MODULE - a group of membrane segments contained in a housing suitable for collecting permeate. Membrane segment connections are external to the housing.

PERMEABILITY - the volume of permeate generated per unit of membrane area, time and pressure across the membrane. (Flux per unit of pressure across the membrane.)

PERMEATE - the fluid that passes through the membrane and thus contains the dissolved materials that pass through the membrane.

PREPARATION RANGE - Several components of equipment arranged to scour and wash fabric (or yarn) in preparation for subsequent finishing operations (e.g., dyeing). The equipment is arranged so that the fabric (or yarn) is drawn through the equipment as a continuous filament.

RECOVERY - the fraction of fluid exposed to the membranes that becomes permeate.

REJECTION - the fraction of a particular material specie that does not pass through the membrane.

SCOURING - the process of cleaning fabric or yarn after weaving or spinning. Scouring usually involves relatively strong cleaning solutions.

SEGMENT - the porous tube lengths connected serpentinely with small radius u-bends. The two ends of the segment protrude through one end of a module for connecting with other segments in the desired system configuration.

SINGLE PASS - a patented (U.S. Patent No. 4200533 of CARRE, Inc.) membrane arrangement such that entering fluid is separated into permeate and concentrate streams without the concentrated fluid ever being routed upstream of a segment of membrane area through which it has passed.

ZOPA MEMBRANE - a high temperature dynamic membrane formed of zirconium oxide/polyacrylic acid membrane (U.S. Patent Nos. 3,431,201; 3,449,245; and 3,503,789).

SECTION 1

INTRODUCTION

In the U. S. about 2 trillion gallons of hot water are discharged by industry each year. Literally about 6% of all the energy consumed by industry goes down the drain. Much of this hot water is "contaminated" with chemicals and other dissolved or suspended material which not only constitute a burden to the environment, but represent an additional "waste" of resources. Thermal and chemical pollution often occur together in industrial effluents.

Caustic solutions are used to clean equipment and products in many industries. A survey of chemicals used in the textile industry (1) indicates that in 1977 approximately one million kilograms of caustic were discharged from cotton preparation processes, much from scouring. Additional caustic was used and recovered by evaporation. The caustic effluent is normally neutralized with acid addition and discharged to a waste treatment plant. The objective of this project was to recover the caustic overflow from a scour saturator that is too dirty for reclamation by existing evaporators.

The current project demonstrates the use of a hyperfiltration (HF) unit to recycle 3 to 10 weight percent caustic (NaOH) at 95°C from a cotton scour saturator. The feasibility of the current application of caustic cleanup and direct recycle was first recognized in a survey of potential applications of high temperature formed-in-place HF membranes in the food industry (2).

This project is funded by a cooperative agreement between the Environmental Protection Agency and CARRE, Inc. The Graniteville Company has provided the capital equipment and the evaluation in production. The improvement of the scouring and mercerization process demonstrated during this project is further described in U. S. Patent No. 4,502,502.

The wide scale implementation of HF to recycle caustic process effluents would have a large impact on pollution abatement. The cost of achieving this pollution abatement with HF will be offset by the combination of savings from the simultaneous recovery of energy and caustic. The pay back period of approximately one year has been shown during this project. In addition the subsequent waste treatment of the concentrated contaminants may be improved because of the reduced volume of the waste stream.

HYPERFILTRATION

Hyperfiltration is a membrane separation process utilizing a semi-permeable membrane. It is also known by the term "reverse osmosis." Permeation through the membrane is driven by pressure differential. Since the separation is achieved without a change of phase, membrane separation is inherently more energy efficient than processes which require a phase change such as evaporation and refrigeration. The optimized Single Pass arrangement (U. S. Patent No. 4,200,533), which requires no recirculation of any concentrated material, requires only approximately 10 BTUs of energy per kilogram of solvent passing through the membrane. The energy used is primarily electrical energy to operate the high pressure pumps. Converted to the equivalent thermal energy on the basis of 10,500 BTU/kilowatt hours, the energy required is approximately 30 BTU's per kilogram of solvent separated. Change of phase technologies, such as freezing and evaporation, require 4 to 40 times as much energy per kilogram of solvent separated.

Initial interest in membrane separation was largely directed to desalination of sea and brackish water. Attempts to utilize the technology in industrial situations encountered restrictions due to the inability of commercially available equipment to tolerate the high temperature and corrosive composition of the typical industrial waste streams. The innovation of zirconium oxide/polyacrylic acid (ZOPA) membranes (U. S. Department of Energy Patent No's: 3,431,201, 3,449,245, and 3,503,789) formed in place on sintered stainless steel tubes (NASA Patent Pending), relaxed many of the limitations. Formed-in-place membranes can be tailored by selection of materials which operate under a wide range of corrosive conditions at high pressures and temperatures, withstand high suspended and dissolved solids, and are not subject to bacterial deterioration. ZOPA membranes were utilized in the prototype HF system studied in this project. Subsequently other HF membranes were developed and the new type are being incorporated in the operating units.

PREVIOUS STUDIES

Five previous studies led to this project. The first study (3), begun in 1972, involved the pilot-scale separation of composite wastewater from a beck dyeing process and a full-scale reuse of hyperfiltration permeate and concentrate. Polyamide (hollow-fine fibers), cellulose acetate (spiral and tubular), and ZOPA membranes on porous ceramic tubes were used. Eighteen production dyeings involving a total of 1348 meters of cloth were carried out in production. The purified permeate water was a satisfatory substitute for normal process water in all production dyeings for water recoveries ranging from 75 to 90%. Membranes used in the renovation of the wastewater had conductivity rejections of 65 to 95% and color rejections from 86 to >99%. It was also technically feasible to reuse all the concentrate. In eleven production dyeings, over 700 meters of cotton velour fabric were produced, graded as first quality and sold commercially. In 10 tests standard shades were produced with an average dyestuff savings of 16%.

The second study (4) involved composite wastewaters obtained from several dyeing and finishing plant processes. These were separated by hyperfiltration, and the cumulative permeate and concentrate of 90% recovery was tested for reuse as process water in laboratory dyeing. Precast and formed-in-place membranes were used at eight dyeing and finishing plants. The processes encountered were: dyeing of nylon using pre-metalized dyes, dyeing of acrylic fabric using basic dyes, and the scouring, desizing and dyeing of cotton and polyester. In all cases the resulting water was acceptable for replacement of process water as determined in laboratory dyeings using standard production evaluations.

The first two studies dealt with renovation of the composite wastewater from the dyeing and finishing plants. Because of the obvious advantages for chemical reclamation and energy conservation, a third study (1) evaluated hyperfiltration for direct recycle of unit process effluents. Five major water and energy consuming preparation and dyeing processes were studied with high temperature hyperfiltration membranes. The permeate produced by the membranes was again found to be universally usable as process water. In some cases the reuse of the concentrate from the individual process effluent streams was estimated to be practical.

The recycle of hot process water and the reuse of dyes renovated from the effluents from a multi-purpose dye range by formed-in-place HF has recently been demonstrated under a multi-agency cooperative agreement (5).

A study was funded by the Department of Energy (2) to survey the food processing industry for possible applications of high temperature formed-in-place hyperfiltration membranes. As part of the study, laboratory tests were conducted with caustic solutions used to peel peaches, pears and tomatoes. The results of this research with caustic solution led to the pilot tests with cotton preparation caustic effluent considered in the current project.

PURPOSE AND SCOPE

The purpose of this project was to demonstrate the use of hyperfiltration to renovate for recycle the caustic effluent from a cotton scour saturator.

An HF recovery system was coupled with a full scale preparation range and operated for over 12 months, during which time a determination of operating costs and technical feasibility was made.

METHOD OF STUDY

Preliminary work leading to this project was divided in two phases. The first phase was laboratory scale membrane performance testing to determine if permeate of satisfactory quality for reuse could be generated at sufficient rates to warrant further testing. The second phase of work was

pilot testing involving 10 square meters of membrane area using fresh process effluent from the preparation range. The pilot plant provided information used to design the prototype recovery system.

The membrane area of the pilot plant was increased from about 10 square meters to about 100 square meters to provide sufficient capacity to process all the effluent from the scour saturator on one preparation range used with cotton fabrics. The expanded pilot unit is the prototype unit that is the subject of this report.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The conclusions that can be drawn from the results of this project are:

1. Hyperfiltration is being used to recycle overflow caustic from a cotton scour saturator. Recycle results in greater than 80% reduction of caustic discharged from the saturator to drain.

2. The hyperfiltration equipment is made of 316L sintered stainless to withstand the harsh environment of caustic system (6% NaOH at 95^{o}C).

3. Although the membrane flux drops off during an operating period, it is restored by routine washing. Long-term membrane performance is maintained by reforming the membrane in place as needed.

4. Use of recycled caustic causes no apparent detrimental effects on the processed fabric.

5. There is no detectable buildup of contaminants in the saturator liquor due to the recycle.

6. The turnkey installation cost (1985) of the system is $361,500. The net savings, above operating costs, resulting from conservation of energy and caustic are $342,000 per year.

It is recommended that the potential for the use of membranes to renovate highly caustic cleaners in other industries be determined. If there is a significant potential for environmental protection determined, it is further recommended that the technical feasibility be determined for selected major industry applications by controlled tests.

SECTION 3

TEXTILE PROCESS DESCRIPTION

The major discharge of caustic (NaOH) from the Gregg Finishing Plant of Graniteville Company is from preparation of cotton fabric. The cotton contains natural contaminants and warp sizing applied during weaving which must be removed before dyeing (6). The order of preparation steps is (a) desize, (b) scour, (c) mercerize, and (d) bleach. The discharges of caustic are primarily overflow from the scour saturator and the solution "dragged out" of the scour saturator on the wet fabric. The caustic drag-out is subsequently washed from the fabric in counterflow washers and discharged as hot wash water at about 1% NaOH. This report section describes the continuous preparation range equipment and function, the caustic flow, production characteristics, and effluent characteristics.

PREPARATION RANGE EQUIPMENT AND FUNCTION

The sequence of operations used to prepare fabric for bleaching and subsequently for dyeing are shown in Figure 1, page 7. Brushing and flame singeing operations precede the wet processes. Following the flame singeing, the fabric passes through the desize saturator, a steam chest and washers. The chemicals applied to the fabric in the desize saturator may be enzyme, stabilized peroxide, or acid depending on the type of warp sizing to be removed. Caustic is used in the desize saturator for pH control only and is not significant for recovery consideration. The steam chest provides the time at controlled temperature for the chemicals to be effective in the desize operation. The desize washers are arranged in counterflow. The washing uses hot water at a flow rate of about 100 liters per minute.

Fabric from the desize washers passes through a set of squeeze rollers at the entrance to the scour saturator. The scour saturator contains 7.5 cubic meters of a caustic solution intended to remove various contaminants from the fabric. The scour solution is maintained at a concentration ranging from 6 to 10% NaOH, depending on the fabric type.

Detergent and chelator are supplied to the scour solution in proportion to the weight of fabric. Strong (40% NaOH) caustic is added to the scour solution to maintain the desired caustic concentration. The caustic concentration is diluted by the water on the incoming wet fabric and with the chemicals which are added as relatively dilute solutions.

Reaction time is achieved by alternately rolling and unrolling 500 meter segments of fabric on cyclinders partially submerged in the saturator

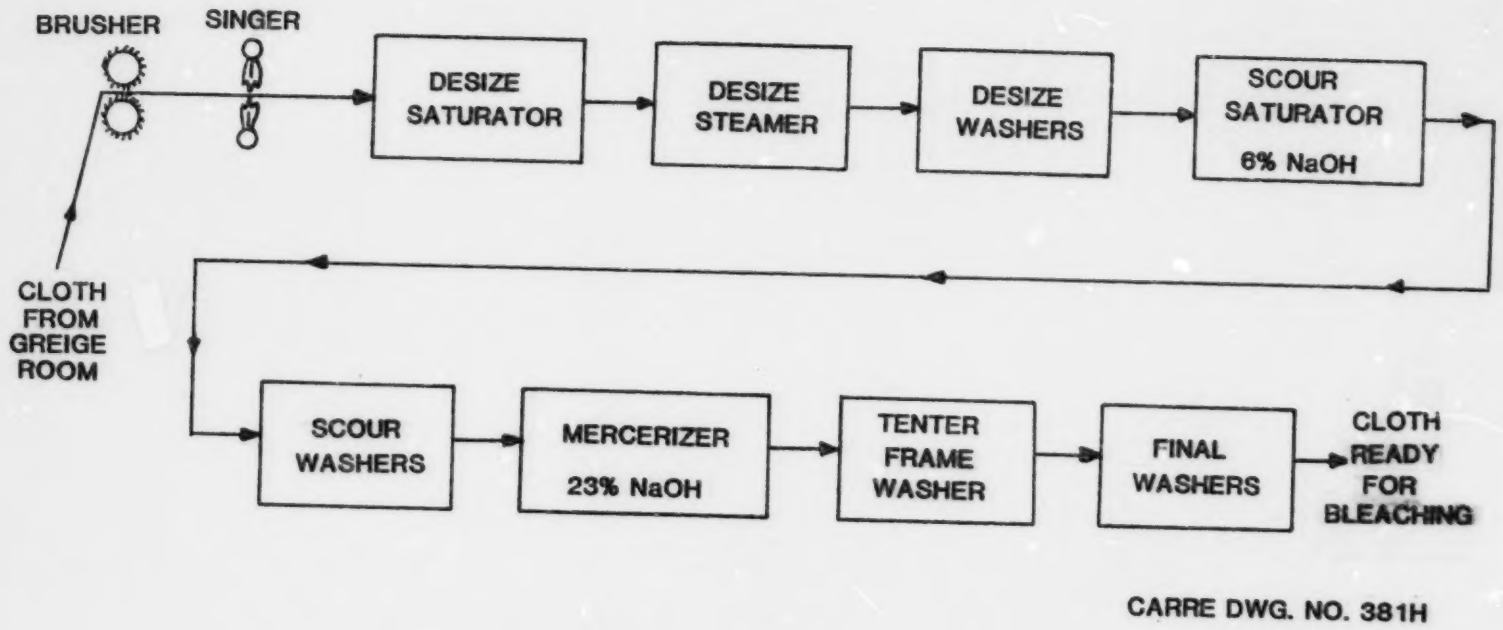

Figure 1. Preparation Range No. 4.

solution. This procedure allows an hour residence time for the fabric in the boiling scour solution.

Steam is supplied to submerged heat exchanger coils to maintain the solution at >95°C. The steam condensate is returned to the boiler and does not dilute the saturator solution. There is a large loss of water vapor from the hot fabric and the 20 square meter surface of the saturator.

An overflow of about 22 liters per minute is maintained to limit the buildup of contaminants in the scour solution. This overflow rate is balanced by supplying "weak caustic" - wash water from the mercerization process (5% NaOH). The flow rate of all chemicals added to the scour saturator is controlled automatically. The overflow rate is inferred by maintaining the caustic concentration and the liquid level in the saturator.

During a test period just prior to initial operation of the prototype HF unit, the overflow rate was established empirically by plant personnel. Years of experience had developed a qualitative criterion for draining and cleaning the saturator of sediment and lint. The irregular interval for draining was usually between 6 and 8 weeks. After draining and cleaning, the saturator is charged with weak caustic.

Following scouring, the fabric segments from the saturator are sewn together and pass through a series of wash boxes. About 100 liters per minute of hot (70°C) process water is supplied to these counterflowed washers. The washers are about 80% effective so that the fabric leaves the washers saturated in about 1% caustic (NaOH) solution.

The mercerizer saturator is automatically maintained at about 20% NaOH by controlling the addition of 40% caustic. Because of the water brought into the saturator with the wet fabric, an overflow necessarily results from the addition of sufficient 40% caustic to raise the solution to about 20%. This overflow is mixed with the wash water from the tenter frame.

The fabric from the mercerizer passes through a tenter frame washer. The fabric is stretched mechanically between clamps that are mounted on chains. The fabric is thus held dimensionally stable as it moves at a controlled speed through the washing section. The washing is accomplished with about 100 liters per minute used serially in four stages arranged in counterflow.

CAUSTIC FLOW SCHEMATIC

The major flows of caustic on the preparation range are shown in Figure 2, page 9. "Strong caustic," 40% NaOH, is added in the scour saturator and the mercerizer saturator to control the caustic concentrate needed for individual types of fabric. This strong caustic is generated by mixing purchased 50% NaOH solution with concentrate (about 35% NaOH) from an

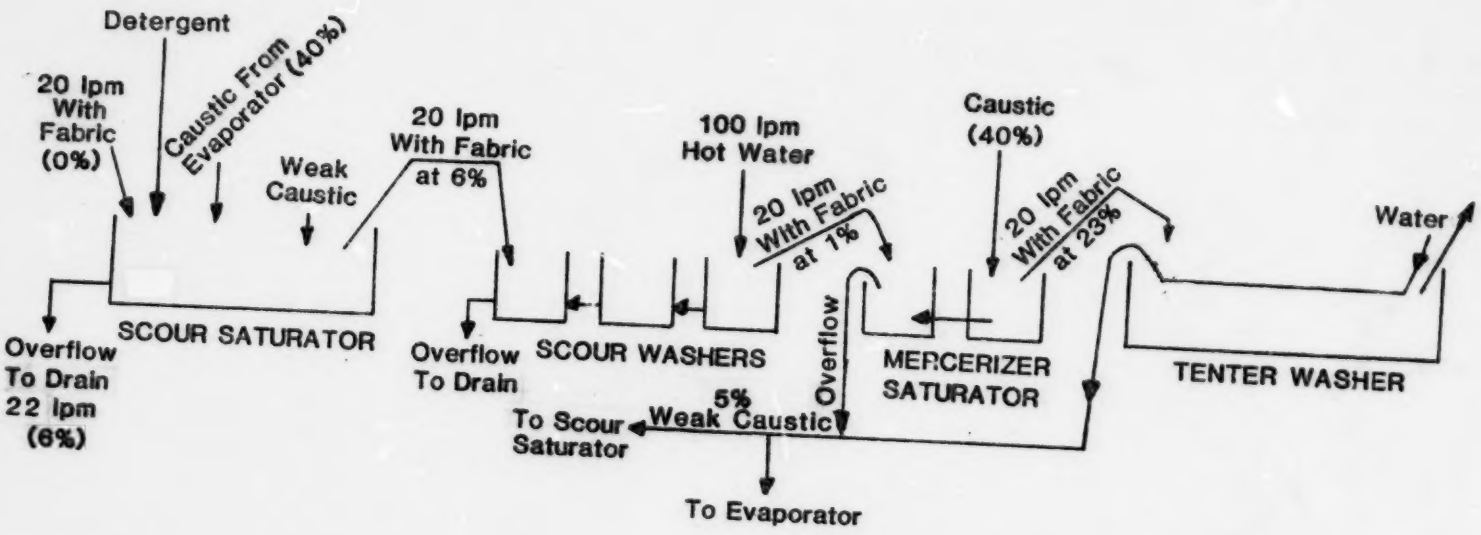

Figure 2. Caustic Flow on the Preparation Range Without Recovery System Interaction.

evaporator. The evaporator feed-stock is the "weak caustic," about 5% NaOH mercerizer wash water.

The closed-loop recycle of caustic is incomplete because of the caustic overflow and drag-out from the scour saturator. Some caustic is also lost on the fabric exiting the tenter washer. Experience has shown that the overflow from the saturator is too contaminated to be processed by the evaporator. The drag-out is diluted in the scour saturator washers to about 1% NaOH and is thus uneconomical to recover by evaporation. Some weak caustic is supplied to the scour saturator to cause the desired volume of the overflow. Strong caustic is added to maintain the caustic concentration in the scour satuator. It is necessary to purchase caustic, 50% NaOH solution, to replace the caustic lost from the scour saturator and the tentor washers.

PRODUCTION

Records of fabric production are routinely maintained. These records include production yardage and percentage of various styles comprising the total production. Production records also include the amount and use of strong and weak caustic, detergent, steam and water for each production lot. The production records include data on the number of quality defects attributed to preparation. The records for the period of this project indicated no significant changes in any production parameter except the amount of caustic and steam used.

EFFLUENT CHARACTERISTICS

The effluent from the scour saturator is not routinely monitored; therefore, no baseline exists for characterization over an extended period. Samples of scour saturator effluent were taken during a period before implementation of recycle. These samples were collected during a period beginning with the filling of the saturator with weak caustic mercerizer washwater. The samples were collected at frequent intervals for three days. The frequency of sampling decreased to weekly for three weeks of continuous operation. The analyses for selected chemical parameters for four samples are presented in Table 1, page 11.

The results of the analyses of these samples show that the various non-caustic components increased to steady-state values within 20 hours. Thereafter the values fluctuate slightly apparently due to variation in the fabric being scoured. The sharp decrease in iron concentration for the 120 hour sample is not understood.

The alkalinity for all samples confirm the controlled concentration of hydroxide at about 7%. The total solids increases rapidly from about 7% to between 10 and 12%. The suspended solids rise rapidly to about 1% but the balance of the non-caustic solids were not identified. Both the B.O.D. and the C.O.D. increase rapidly with the C.O.D. being much higher.

Table 1. Chemical Characteristics of Scour Saturator Overflow Effluent

Assay (mg/l)	Time of Sample Collection[1] (hrs) 0	20	32	120
Total Solids	74,200	122,200	128,500	107,400
Suspended Solids	1,530	4,980	9,060	6,200
C.O.D.	3,000	45,800	51,500	37,300
$B.O.D._5$	110	15,000	13,600	12,200
Alkalinity (Carbonate)	3,400	6,830	8,540	6,840
(Hydroxide)	64,900	72,600	71,800	70,900
Phosphate	660	440	460	430
Oil and Grease	610	660	2,050	1,100
Petroleum Hydrocarbons	30	50	100	50
Calcium	0.4	1.9	1.7	2.5
Iron	16.3	10.0	15.0	2.5
Magnesium	3.2	11.8	11.8	12.0

(1) Time of sample collection is measured from time production began after the saturator was cleaned and refilled with weak caustic.

SECTION 4

RECOVERY SYSTEM

The recovery system was designed to transfer fluid from the overflow point of the scour saturator tank to the HF unit and return the renovated permeate directly from the pressurized HF modules to the scour saturator. The return point is at the opposite end of the saturator tank from the point of overflow. The concentrate from the HF unit is passed to the plant drain system.

The details of the equipment arrangement have evolved throughout the project period. In the discussion which follows, the design arrangement in use at the time of writing is presented. The HF units are being modified as their capacity is expanded.

The operating procedures of the recovery system are also evolving. The practice at the time of the writing is presented.

SYSTEM SCHEMATIC DIAGRAM

A schematic diagram of the recovery system equipment is shown in Figure 3, page 13. A small centrifugal transfer pump withdraws fluid from the saturator tank at the point of overflow. About 100 liters per minute are withdrawn through a coarse filter, with 10 mm openings, and pumped to an elevated (about 3 meters above the level of the system pumps) vibrating 100 mesh screen filter. This filter removes strings, lint and other large particulate matter. The solids are discharged into a container and the liquid passing through the screen collects in a small 20 liter reservoir. Approximately 55 liters per minute of liquid flows by gravity from this small reservoir to the HF unit high pressure pump. The remaining liquid (45 liters per minute) overflows directly back to the scour saturator.

The high pressure pump for the HF unit is a multi-stage centrifugal unit capable of about 100 liters per minute at 6.8 M Pa with a 30 hp motor. The output of the pump is throttled to match the capacity of the HF membranes. At nominal operating conditions the high pressure pump delivers about 55 liters per minute to the membrane modules, 12 liters per minute of concentrate is discharged to the plant drain and 43 liters per minute of HF permeate is returned to the saturator.

Weak caustic is supplied to the saturator tank to replace the HF concentrate. Additional weak caustic is added to the scour saturator and the overflow is opened when the HF unit is not operating at full capacity.

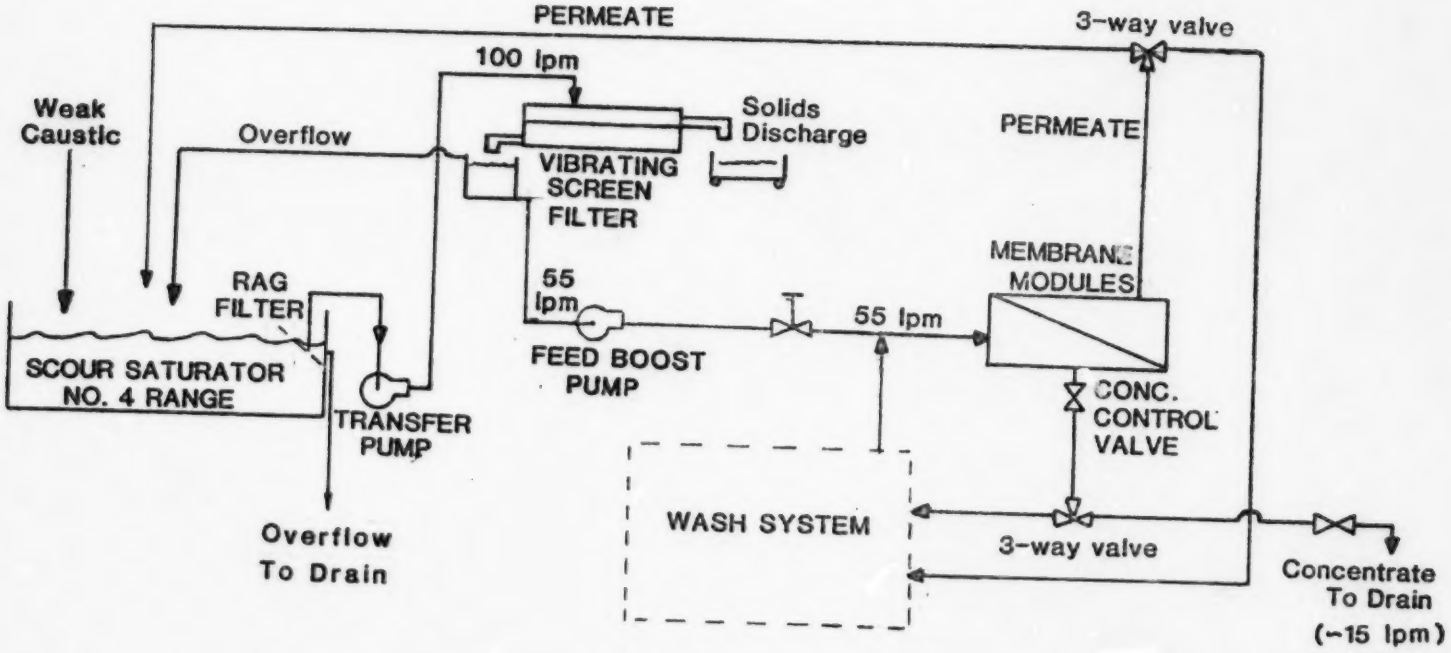

Figure 3. Recovery System Interaction With Scour Unit

There is a separate system of pumps and reservoirs for washing and reformation of membranes. This system is described below.

HF MEMBRANE ARRANGEMENT

The HF membrane configuration is shown schematically in Figure 4, page 15. There are eleven modules containing either 5/8-inch or 1/2-inch internal diameter porous sintered metal tubes. These modules are connected to two headers in such a manner that the flow path can be selected in any combination from eleven in series to eleven in parallel. This arrangement also permits operating some of the modules while others are isolated for cleaning or reformation of membranes.

The headers give maximum flexibility in module arrangement. This flexibility was particularly valuable in the study of velocity effects during operation and cleaning.

OPERATION MODES

During the daily washing routine the high pressure pump is isolated. The high pressure pump is made of a high nickel alloy and must be isolated from the acid washing solution. The washing utilizes stainless steel positive displacement pumps. The same pumps used for washing were used for in-place formation of the HF membrane.

RECYCLE

When the HF system is processing overflow from the scour saturator tank, the amount of weak caustic supplied is controlled to maintain the proper liquid level in the tank. Much of the time that the HF unit was operating, caustic addition to the saturator was equal to the concentrate flow. At other times, e.g., during equipment maintenance periods and during each daily washing sequence, there was no recycle from the HF and the amount of weak caustic flow was increased to maintain an acceptable quality of caustic in the scour saturator. This interruptible reuse did not in any case cause production problems or variations. Because interruptions in recycle were permissible it was possible to develop much information that would have been otherwise impossible with the initial equipment problems.

A reuse scenario was developed and will be followed with the full scale system scheduled for startup in late 1985. The reuse scenario is:

(1) The most contaminated fluid from each of the scour saturators (currently four) will be transferred continuously through a 100 mesh vibrating screen to a holding tank. The enlarged HF unit will process about 80 liters per minute with about 12 liters per minute being discarded and 68 liters per minute being transferred to a permeate reservoir. The scour saturator tank will be supplied from this permeate reservoir.

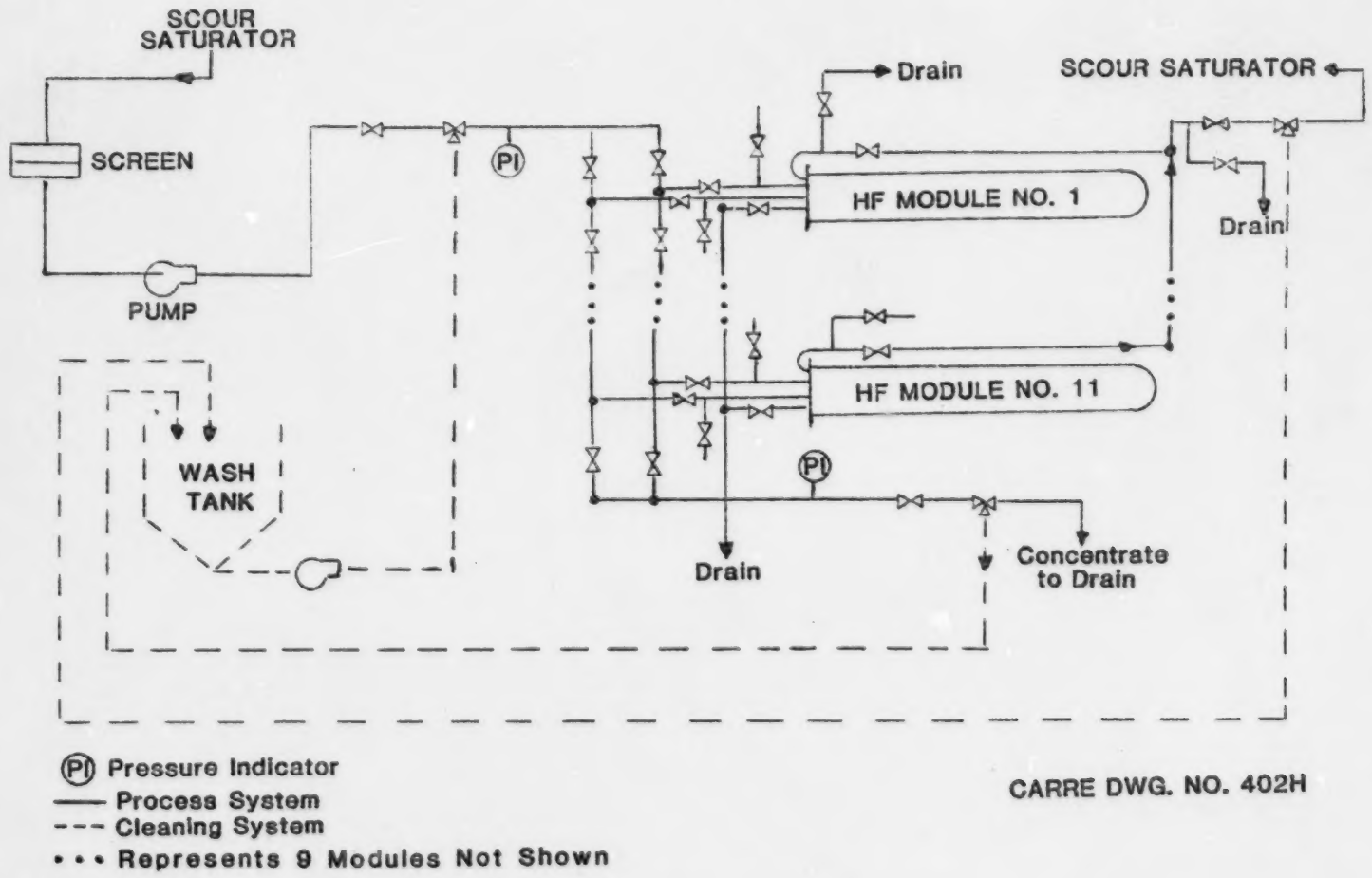

Figure 4. HF Membrane Configuration

(2) Once each day the HF unit will be shut down for cleaning. The reservoirs are designed to permit continuous operation of the saturators without sending material to the drain. However, the system is designed so that overflow to drain and an external supply of caustic are available.

CLEANING

The schematic diagram of the washing equipment is included in Figure 4, page 15. The washing solutions are pumped from a mixing tank through the headers and hence the selected modules. Individual modules were cleaned by utilizing flexible piping for connection to the washing pumps and reservoir. The same arrangements were used for membrane in-place formation.

Two types of washing solutions are used. A caustic solution of similar composition to the scour solution is used to remove organic foulants. The second solution is a slightly buffered solution of acetic acid for removal of inorganic precipitants.

SECTION 5

PROJECT RESULTS

MEMBRANE AND EQUIPMENT PERFORMANCE

The performance of the recovery system is evaluated in terms of the quantity of caustic (NaOH) recycled. The limitations on recycle are the amount of permeate produced and the quality of the scour saturator fluid in terms of any effects on fabric quality.

The results of chemical analyses of the scour saturator fluid before and during operation of the recovery system are presented. The experience with membrane fouling and cleaning is presented.

CHEMICAL CHARACTERISTICS OF RECYCLED PERMEATE

A quantitative evaluation of permeate quality was attempted using a turbidimeter and a spectrophotomer. Neither instrument provided useful data because color in the sample interferred with turbidity measurements and color measurements could not be correlated. The color, thought to be primarily caramelized sugars, was not rejected completely by the membranes and thus provided no useful data on system performance.

The chemical characteristics of the scour saturator fluid were determined by comparison of the analyses results for a series of samples collected before and during operation of the recovery system. Each series of samples were collected after the scour saturator had been drained, cleaned and refilled with weak caustic. Each sample series covered about three weeks of operation.

The concentrations of selected species in the scour saturator overflow effluent are presented in Figure 5 (a, b), page 18 and 19, for the period before operation of the recovery system was initiated. Similar results are presented in Figure 6 (a, b), page 20 and 21, for a corresponding period during operation of the recovery system. In parts (a) of Figures 5 and 6, the results for total solids, C.O.D. and magnesium are presented. There are no apparent differences in the concentration levels of these parameters resulting from the use of the recovery system. In parts (b) of these figures, the results for zinc, iron and suspended solids are presented. Again, there are no apparent differences with the possible exception of suspended solids. The suspended solids concentration may be less during recycle.

The operation of the recovery system permits the substitution of HF permeate for weak caustic to maintain an equivalent quality of fabric

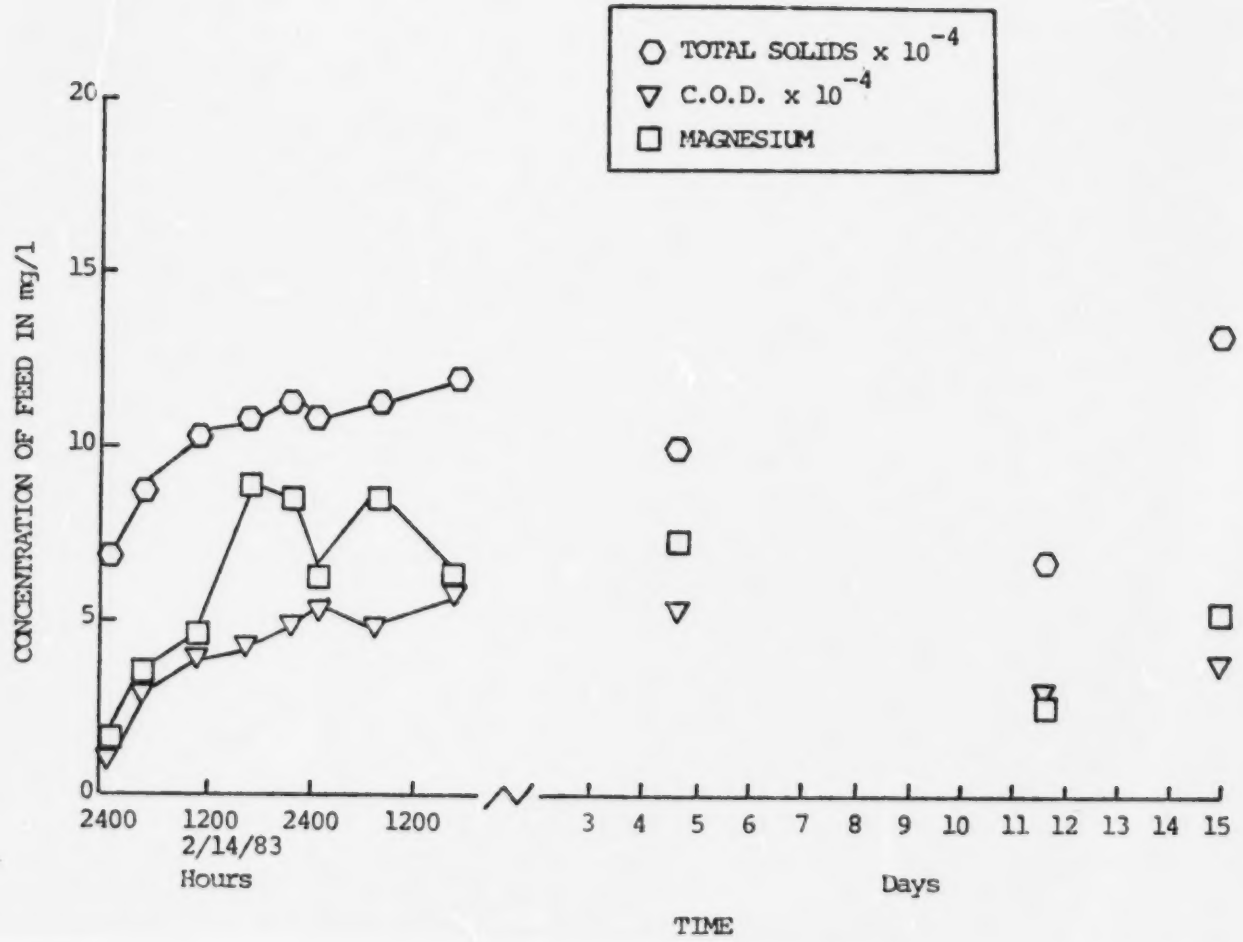

Figure 5(a). Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken Prior to Recovery System Operation.

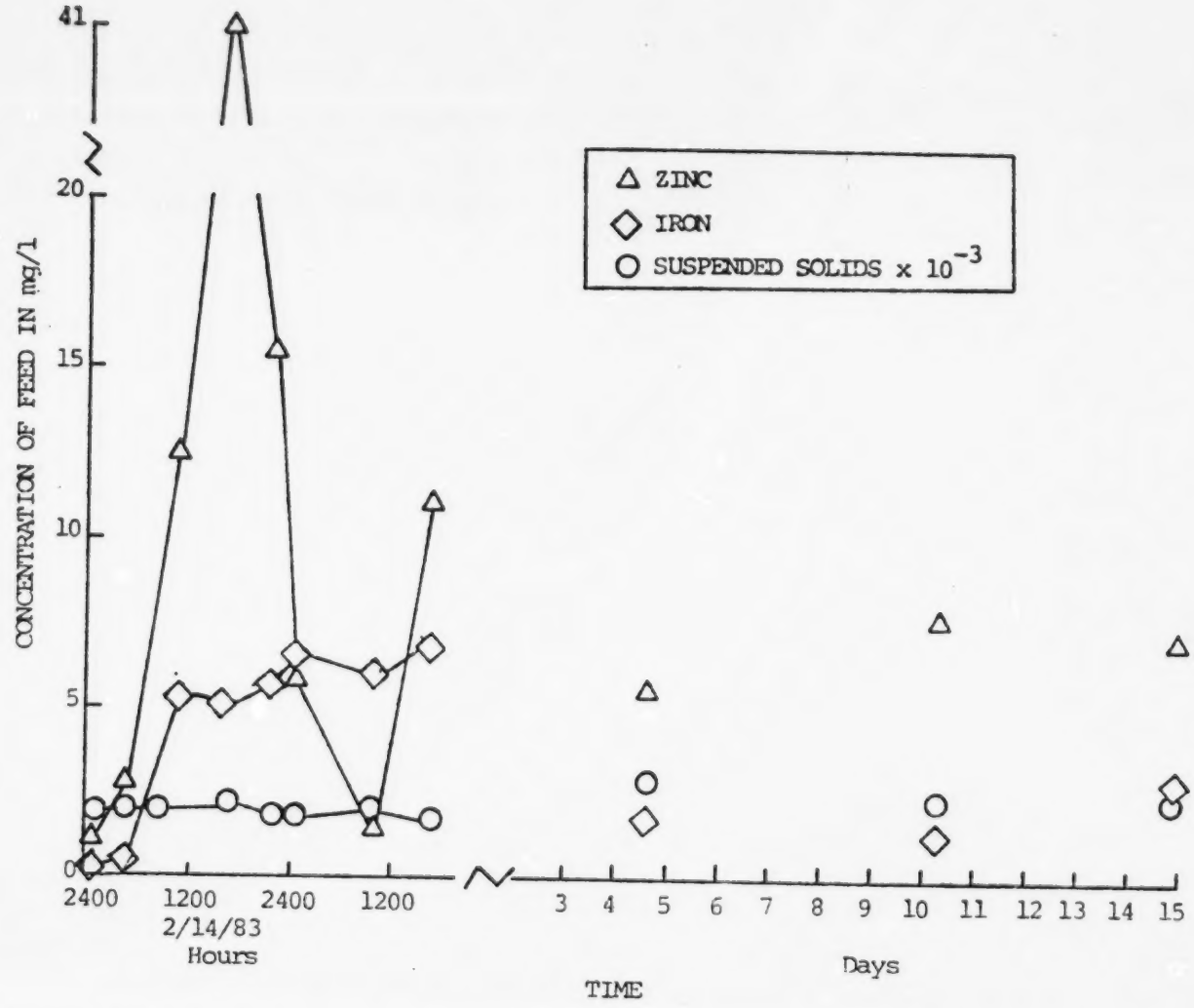

Figure 5(b). Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken Prior to Recovery System Operation.

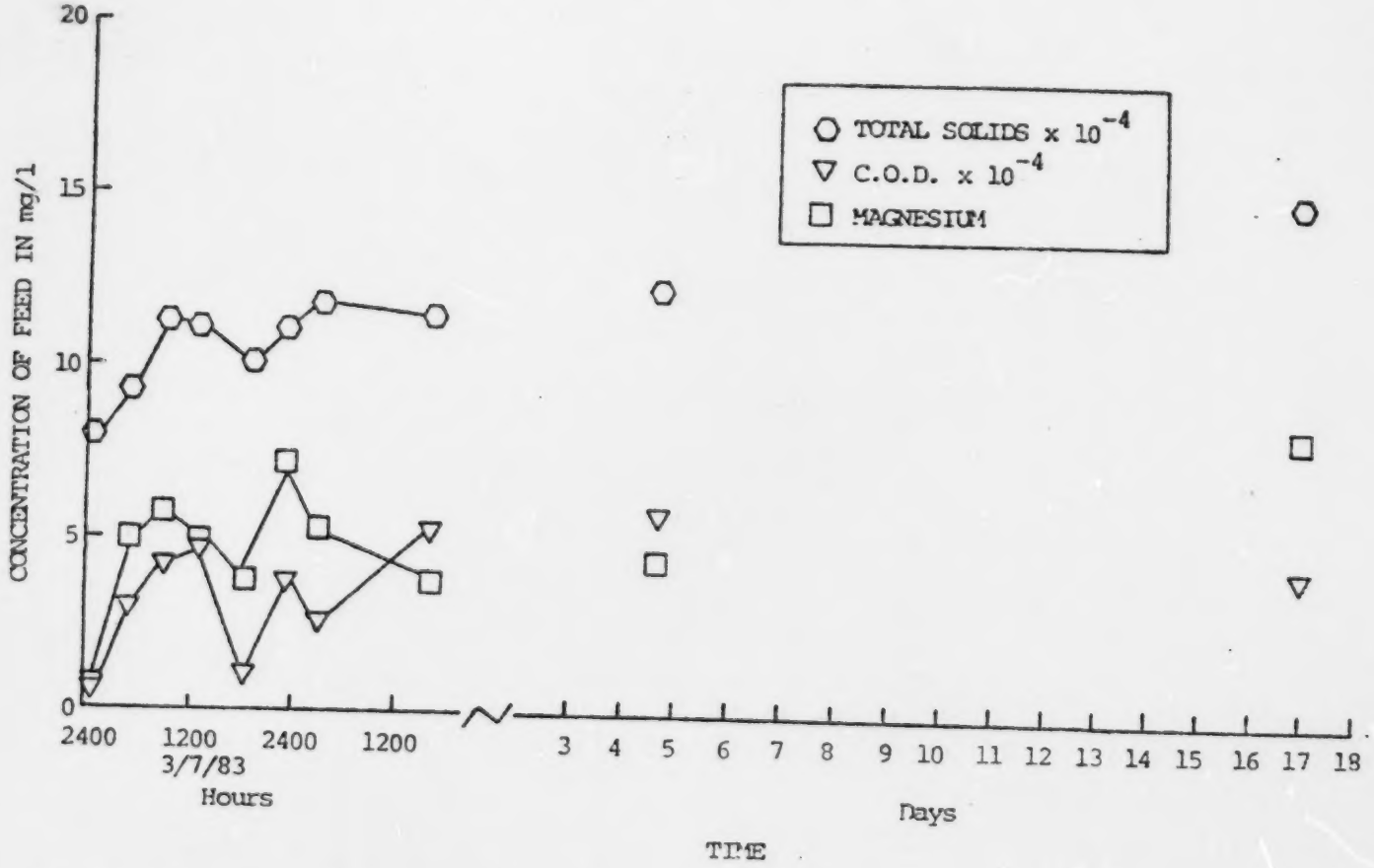

Figure 6(a). Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken During Recovery System Operation.

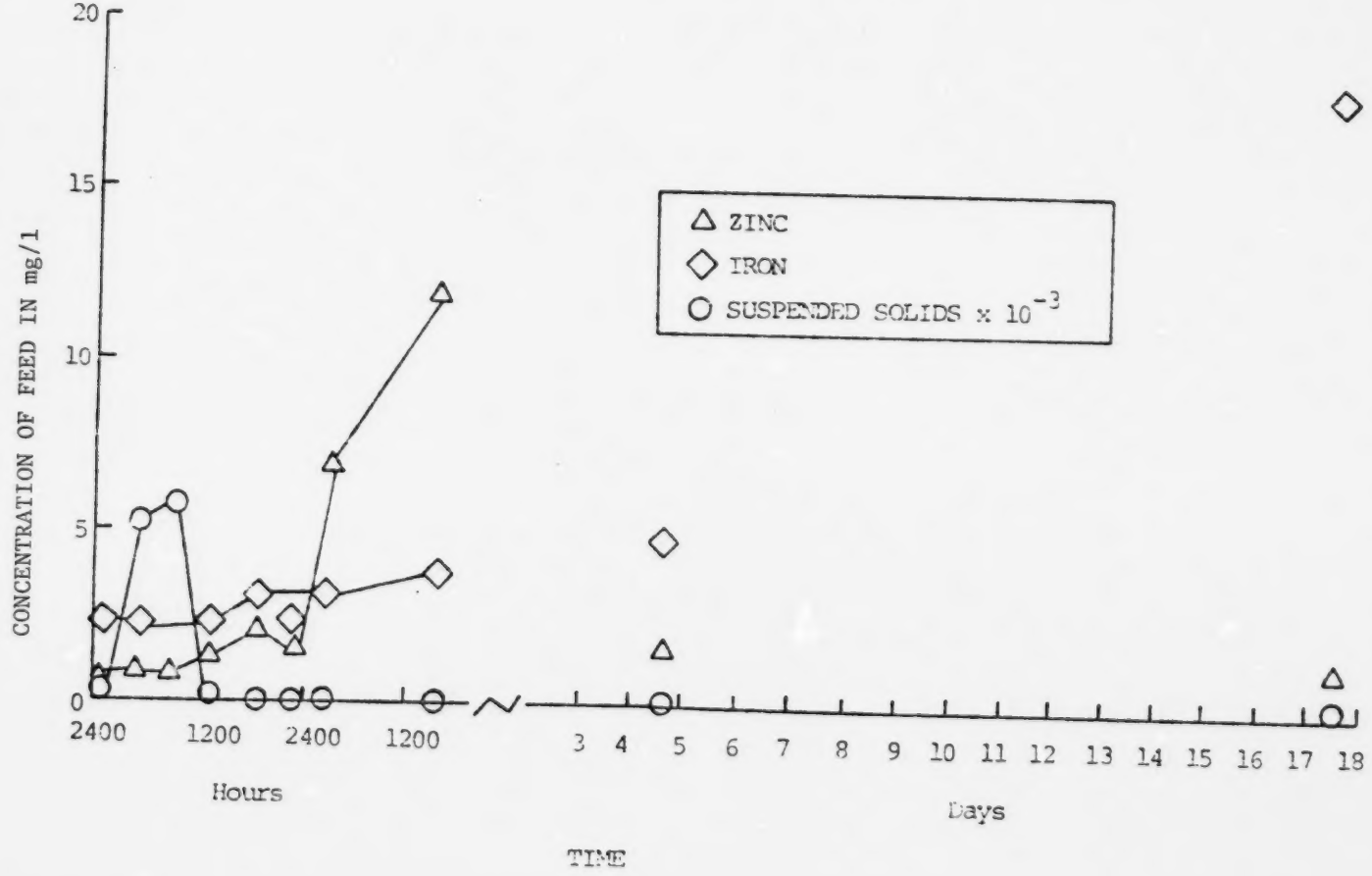

Figure 6(b). Scour Saturator Fluid Component Concentration versus Operating Time. Data Taken During Recovery System Operation.

preparation. The chemical analysis results presented above seem to confirm that the saturator solution is not significantly affected by operation of the recovery system. The accuracy of the chemical analyses, judged by mass balance considerations, was not, however, sufficient to determine membrane rejections or to calculate changes in the composition of the fluid.

MEMBRANE FLUX

The quantity of fluid recycled is the accumulation of the permeate from all the available membrane area. The permeation rate per unit area is defined as flux; cubic meters/square meters per day or m/d. The flux is a function of instantaneous operating conditions and accumulative effects of fouling and chemical interactions with fluid constituents.

The principal conditions that influence the flux are pressure, temperature, contaminant concentration, fluid velocity and membrane condition. In the present application, the pressure is approximately constant. The scour process temperature is fixed at about 95°C. The contaminant concentration varies with the type of fabric. The velocities are determined by the HF unit configuration. Consequently, the influence of operating variables was considered in the design of the recovery system, but, cannot be used for control of performance.

Membrane fouling is defined as a decrease in flux that is not a reversible effect of operating variables. Fouling is usually categorized as (a) an alteration in the membrane due to chemical reaction or (b) an accumulation of a deposited layer of material.

In the present application, the fouling mechanisms are thought to be:

(1) accumulation of waxes, warp sizes, starches and partially dissolved cellulosic material, and

(2) accumulation of inorganic oxides, carbonates, or hydroxides.

The performance during a selected week, is presented in Table 2, page 23. This week was selected because the membrane performance was typical and no equipment related problems occurred. The permeate flow rate is presented beginning with day 1 just after the membranes had been formed in place. Each day the permeate flow was recorded just before and just after washing. An additional observation is recorded during the day, usually after about 4 hours of operation. The washing takes up to four hours, so the daily operating period is from 20 to 22 hours.

Each day there is a decrease in permeability that is generally restored by washing. The daily cleaning period has been decided upon to establish a regular routine to be consistent with a regular plant routine. Efforts are continuing to improve these operating requirements however.

It was thought that the type of fabric being processed in the scour saturator might influence the rate of fouling. Figure 7, page 24, shows

Table 2. Performance During Selected Five-Day Period

Day No.		Permeate Flow (l/min) 1 hr.	4 hr.	20 hr.
1	Recoat	20	--	14
2	Wash	33	20	12
3	Wash	33	28	14
4	Wash	27	27	19
5	Wash	24	25	--

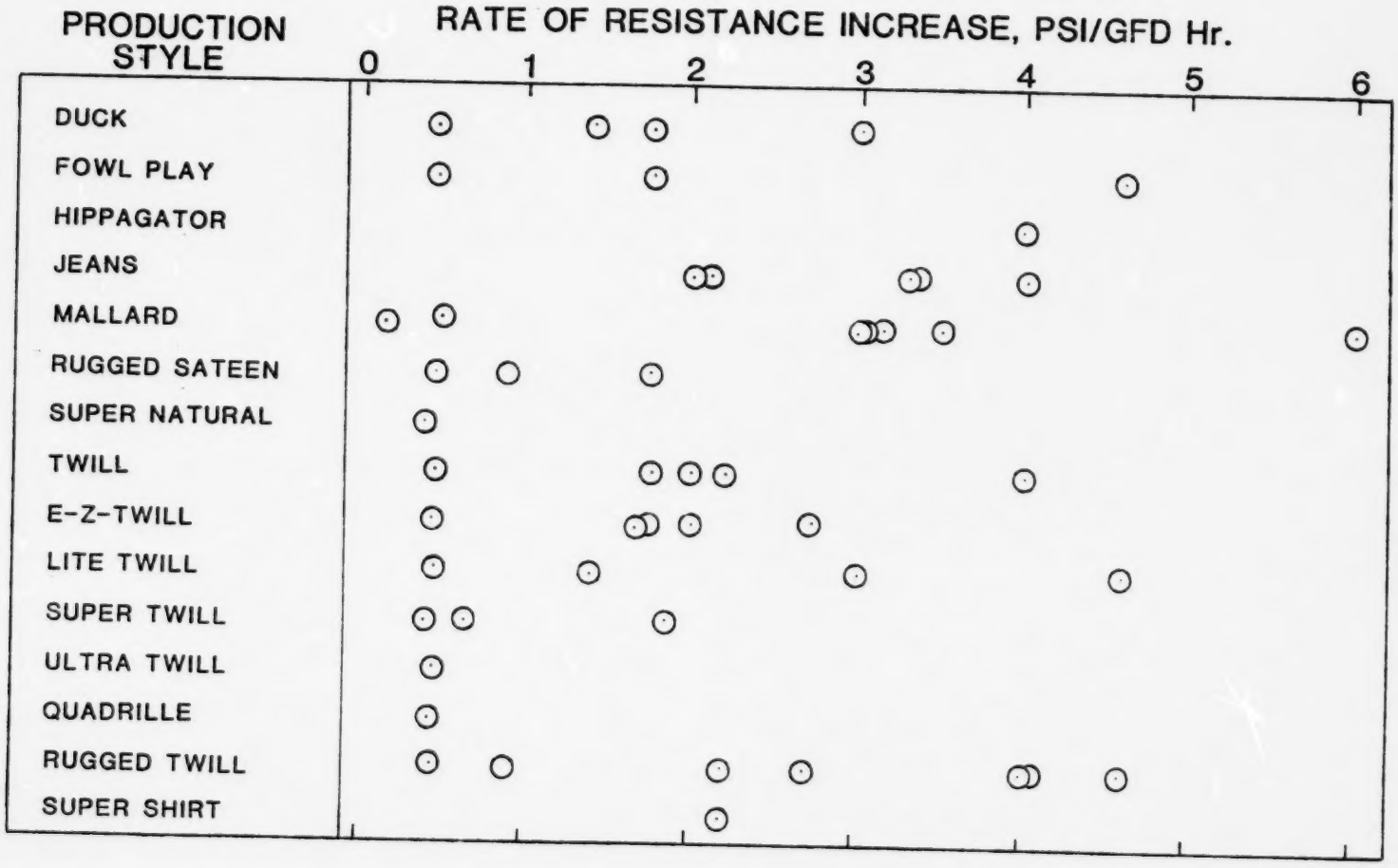

Figure 7. Fouling Rates Versus Production Style.

that there is no correlation between the rates of fouling (rate of resistance increase) and the production style. Both high and low fouling rates have been observed for most of the types of fabric processed.

MEMBRANE CLEANING

In every particular situation, the cleaning procedures are selected to remove the specific foulants. Even the sequence of cleaning is important. For example, an acid flush may precipitate material soluble in base.

The principal foulants in the current situation require both a high pH solvent wash solution and an acid flush. The basic solution is to remove the organic materials and the acid flush is to remove the inorganic precipitates.

The cleaning procedure is presented in Table 3, page 26. To clean the system the high pressure pump is turned off and the HF modules are isolated by closing valves at the scour solution supply and also at the permeate return. The HF modules are drained of permeate, then the system is flushed with the basic (pH >12) cleaning solution. The system is flushed with hot water and then flushed with the acid solutions.

In preparing for recoating, the modules are first cleaned following the standard procedure. Extra cleaning is carried out to strip the old membrane then the new membrane is formed in place. The procedures for recoating are proprietary. Recoating is provided on a routine basis under the technology support contract.

EQUIPMENT OPERATING HISTORY AND AVAILABILITY

A principal reason for the recovery unit being at decreased capacity during the period of this project was a problem with the porous metal membrane support tubing. After this problem was recognized in the summer of 1983, an HF module with an improved design, made of properly prepared 316L stainless steel, was put into service to replace one of the 11 existing modules. After about a year of reliable operating experience, the entire prototype system was replaced with modules made of properly prepared 316L stainless steel.

The other factors influencing HF unit availability are the time required for washing and the time for recoating. Currently the daily washing requires about four hours. The recoating procedure can be scheduled for weekends. However, if it is necessary to do the recoating during production time, there is an additional loss of about 5% of available operating time. Attention is being placed on improving the washing technique since, currently, about half the washing time is required to make up the washing solutions and to bring them to the proper temperature. The cleaning system equipment is being modified to reduce this lost time.

Table 3. Membrane Cleaning Procedure

1. Drain permeate from all modules
2. Fill the 1000 liter wash tank with water and add in order:

   4 liters of weak caustic
   160 milliliters of detergent
   100 grams of trisodium phosphate

3. Heat this solution in the wash tank to $90^{o}C$
4. Pump the solution through the system to drain
5. Repeat steps 2-4
6. Fill the 1000 liter wash tank with water and heat to $90^{o}C$
7. Pump hot water through the system
8. Fill the 1000 liter wash tank with water and add in order:

   500 grams of citric acid
   1 liter ammonium hydroxide (pH = 6.0 ± 0.5)

9. Heat this solution to $90^{o}C$
10. Pump the solution through the system to drain
11. Repeat steps 6-7
12. Start system on scour solution

ABILITY TO REUSE CAUSTIC

The test to evaluate reuse was simple observation of the operation of the saturator in the normal production mode with and without the HF unit in service. This scour saturator coupled with the HF prototype unit was operated on the normal plant production schedule.

EFFECT OF REUSE ON FABRIC

Four sets of fabric samples were collected and measured for contaminants concentration using an extraction procedure in an attempt to obtain a quantitative evaluation of reuse on the effectiveness of the scour-washer combination. The results are shown in Table 4, page 28. Samples were collected upstream and downstream of the scour saturator and downstream of scour washers. The four sets of samples were collected just after the scour saturator was cleaned and filled with fresh weak caustic from the mercerizer wash water ("new caustic" in Table 4) and after three weeks of operation since the last drain and clean of the saturator ("old caustic" in Table 4), both with and without recycle. These data indicate no significant difference in the effectiveness of the scour washers in preparing the fabric for the mercerizer.

Probably these extraction tests are not very sensitive since operating experience over the years has shown it to be beneficial to clean the saturator periodically. The most important test of reuse has been that for more than 12 months the fabric quality was not detected to vary with or without the HF unit in operation. During this period over 3 million liters of caustic was saved and over 15 million meters of fabric was processed when at least a portion of the normal overflow was recycled.

COST EVALUATION

The savings to be realized from recycle of caustic are in two categories; first, direct reduction in production costs; and, second, avoidance of environmental control costs associated with the discharge of caustic.

Table 5, page 29, presents the major savings for the HF renovation and recycle of scour saturator overflow. The total savings of $379,900 (1985) are over 90 percent associated with the value of the caustic and the cost to neutralize it if discharged.

Table 6, page 30, presents the approximate costs of the HF system and its operation. The total costs for the first year are about $399,400, thus providing a simple payout period of about one year. The major operating costs are associated with membrane cleaning and reformation. These costs are relatively reduced for larger systems. Specifically for the larger system being installed for startup in 1985 the membrane cleaning and technology supported costs are being reduced from 12.2 percent of installed capital cost for the present prototype to about 8.4 percent for the larger system.

Table 4. Fabric Extract Chemical Analyses Results

Assay* (mg/l)	NEW CAUSTIC Before Scour Sat.	NEW CAUSTIC After Scour Sat.	NEW CAUSTIC After Scour Washers	OLD CAUSTIC Before Scour Sat.	OLD CAUSTIC After Scour Sat.	OLD CAUSTIC After Scour Washers
Before Recycle						
Total Solids	710	3980	346	488	3040	360
Suspended Solids	90	18	4	114	26	4
C.O.D.	660	740	200	547	860	190
B.O.D.	115	367	75	234	261	59
Alkalinity (Carbonate)	0	2170	20.2	0	800	174
(Hydroxide)	0	570	0	0	200	0
Ash	410	1830	280	350	1850	240
Oil and Grease	6	65	7	4	44	10
Petroleum Hydrocarbons	<1	15	2	<1	10	1
Calcium	0.60	0.60	0.40	0.55	0.60	0.48
Iron	0.3	<0.2	<0.2	<0.2	<0.2	0.2
Magnesium	1.0	0.4	1.0	0.56	1.7	1.7
Sodium	86	1100	140	50	1030	55
Zinc	0.05	0.14	0.04	0.20	0.10	0.04
After Recycle						
Total Solids	883	2390	263	400	3170	1220
Suspended Solids	100	30	4	16	8	8
C.O.D.	1110	790	200	265	870	340
B.O.D.	300	181	68	64	326	114
Alkalinity (Carbonate)	0	7400	0	<1	730	80
(Hydroxide)	0	0	0	<1	<1	<1
Ash	0	1600	100	395	3140	1200
Oil and Grease	11	40	8	<1	14	<1
Petroleum Hydrocarbons	3	6	<1	<1	5	<1
Calcium	0.72	0.68	0.72	1.7	1.4	0.8
Iron	<0.2	0.2	0.2	0.05	0.07	0.08
Magnesium	1.2	0.9	1.2	2.3	0.10	0.40
Sodium	38	850	43	1400	1850	940
Zinc	0.07	0.06	0.06	0.05	0.05	0.02

*The fabric samples were of a standard size and were washed (extracted) in a fixed volume of fluid. The assay in mg/l thus represents a relative amount of the specie in each case.

Table 5. Annual[a] Savings for Recycle of 40 Liters/Min. of Caustic (6% NaOH)

	Quantity	Value[b]
Direct Production Cost Reductions		
Caustic savings (thousand kg)	900	$250,000
Energy savings[c] (million BTU)	4,120	25,000
Water savings (million liters)	14	1,400
Environmental Control Cost Reductions		
Neutralization[d] (thousand kg)	1,100	$100,000
Waste treatment[e] (million liters)	14	3,500
TOTAL		$379,900

(a) 6000 hours per year
(b) Based on $250/ton of caustic; $6 per million BTU; and 10 cents per 1000 liters of water
(c) Energy savings based on 90°C discharge temperature
(d) Assumes spent sulfuric acid available at 9 cents per kg
(e) Assumes 25 cents per 1000 liters, after neutralization

Table 6. Capital and Operating Costs for Recycle of 40 Liters/Minute of Caustic

Capital Costs[a]	
HF unit	$361,500
Installation	(included)
Operating Costs[b] ($/yr)	
Horsepower (10hp motor)[c]	2,500
Cleaning chemicals	2,000
Labor for cleaning[d]	10,400
Maintenance[e]	5,000
Membrane technology support[f]	18,000
TOTAL	$ 37,900

(a) Turnkey installation
(b) 6000 hours per year
(c) Based on 6 cents/kilowatt-hour
(d) Based on an operator available 4-hour/day at $8/hr. and 30% burden
(e) Based on 5% for non-membrane components
(f) Full cost contract for membrane reformations and update service

REFERENCES

1. C. A. Brandon. Closed-Cycle Textile Dyeing: Full-Scale Hyperfiltration Demonstration. EPA-600/S2-83-027, U. S. Environmental Protection Agency. Research Triangle Park, North Carolina, 1983. PB 83 193219.

2. Work Performed Under U. S. Department of Energy Contract Number DEAC03-79SC40264.

3. C. A. Brandon and J. J. Porter. Hyperfiltration of Textile Finishing Plant Wastewater. EPA-600/2-76-060, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1976. 147 pp. NTIS NO. PB 251-188/AS.

4. C. A. Brandon, J. J. Porter and D. K. Todd. Hyperfiltration for Renovation of Composite Waste Water at Eight Textile Finishing Plants. EPA-600/2-78-047, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978. 237 pp. NTIS NO. PB 279-451/AS.

5. J. L. Gaddis, C. A. Brandon and J. J. Porter. Energy Conservation Through Point Source Recycle with High Temperature Hyperfiltration. U. S. Environmental Protection Agency, EPA-600/7-79-131 (June 1979). NTIS PB 299-183.

6. J. Juby, Dominion Textile Inc. Cotton/Polycotton: One-Step Bleaching. TEXTILE CHEMIST AND COLORIST, May 1985, Vol. 17, No. 5.